

**CONTAMINANTS IN FISH AND CLAMS
IN
SINCLAIR AND DYES INLETS**

Prepared for

Dr. Fran Solomon
Northwest Regional Office
Washington District of Ecology

by

James Cubbage

Washington State Department of Ecology
Environmental Investigations and Laboratory Services
Toxics, Compliance, and Groundwater Investigations Section
Olympia, WA 98504-6814

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ABSTRACT

Sinclair Inlet and Dyes Inlets are located adjacent to Bremerton, an intermediate-sized city with a sizable shipyard. Earlier studies have shown elevated concentrations of contaminants in sediments of these inlets. To evaluate accumulation of these contaminants in marine organisms, bottom fish and clams from several sites in these two inlets were collected and analyzed in 1989, 1990, and 1991. Compounds of interest included metals (arsenic, chromium, copper, lead, zinc, mercury, silver, and cadmium) polycyclic aromatic hydrocarbons (PAH), butyltins, and chlorinated hydrocarbons. All data were eventually of acceptable quality, though some metals data were qualified.

Little geographic pattern was apparent for metals concentrations in fish or clams. Fish had higher concentrations of arsenic, lead, and mercury than clams. The highest metals concentrations in fish were: arsenic: 21.1 mg/kg; lead: 4.5 mg/kg; and mercury: 0.39 mg/kg (all wet weight basis). The highest metals concentrations in clams were cadmium (25 mg/kg); silver (0.64 mg/kg); copper (19.8 mg/kg); and zinc (25.1 mg/kg) (all wet weight basis). With the exception of DDE reported in fish from Site 7 at 1.8 $\mu\text{g/kg}$ (wet weight), no pesticide/PCBs were found in fish or clams in this study. Quantitation limits for PCBs were high. No PAHs were found in fish above the quantitation limits. PAHs were found in clams at moderate concentrations. The highest concentrations found in clams were 46 $\mu\text{g/kg}$ total PAH wet weight. The three and four ring PAH predominated in all samples where PAH were found. Low concentrations of butyltins were found in fish and clams. The highest concentration of butyltins was 18.2 $\mu\text{g/kg}$ wet weight.

Chromium, copper, lead, and mercury in fish were higher in this study than in comparable studies in Puget Sound urban bays. In other studies of urban bays, PCBs were reported for all samples except the flathead sole collected in the reference area in Discovery Bay. One possible explanation for the inability to detect PCBs is the low lipid weight reported in the samples. In clams, mean concentrations of the arsenic, cadmium, lead, and zinc were comparable to concentrations from reference areas. Mercury, chromium, and copper concentrations are equivalent to concentrations found in non-reference areas. LPAH concentrations in clams are below those found in smoked foods, but HPAH concentrations found in clams in the present study are equivalent to those found in smoked fish. The total PAH concentration in clams from this study is comparatively low and equivalent to reference areas.

Tentative and rudimentary risk assessments showed a small carcinogenic risk (10^{-5}) from habitual and ample consumption of seafood from the area. The non-carcinogenic risk of regular consumption of fish was low, but could be moderate in worst case situations. These cumulative risk estimates cannot reconcile potential synergistic or antagonistic effects among non-carcinogens.

INTRODUCTION

Bremerton, a city of 40,000, sits on Sinclair Inlet and Dyes Inlet. On the north shore of Sinclair Inlet resides the largest Navy shipyard facility on the West Coast (Puget Sound Naval Shipyard). This shipyard has been an historical source of discharge of numerous contaminants including solvents, heavy metals, and assorted salts used in metal plating, boilermaking, and assorted shipfitting activities (U.S. Navy, 1983). The U.S. EPA contracted with Tetra Tech to review current and historical contamination of Sinclair and Dyes Inlets. From that review, several contaminants including polycyclic aromatic hydrocarbons and heavy metals have been found in sediments in Sinclair and Dyes Inlets at 1-2 orders of magnitude above background concentrations (Tetra Tech, 1988a). Polychlorinated biphenyls (PCBs) have been found at concentrations in Sinclair Inlet sediments at 1-3 orders of magnitude higher than in reference areas (Tetra Tech, 1988a).

The few samples of fish and shellfish tissue collected from Sinclair Inlet show concentrations of PCBs elevated above reference areas (Tetra Tech, 1988a). Arsenic, cadmium, lead, and heavy metals found at elevated concentrations in sediments in Sinclair and Dyes Inlets often bioaccumulate, and are associated with other urban areas. Polycyclic aromatic hydrocarbons (PAHs) are potentially harmful compounds often found in relatively high concentrations in urban sediments. Organotin compounds (butyltin) have been formulated in hull paint to deter biofouling and have been found in the water column in Sinclair Inlet (Grovhoug *et al.*, 1987). These compounds are toxic and can bioaccumulate. The Tetra Tech report concluded that data on bioaccumulation of organic compounds and metals in organisms from Sinclair and Dyes Inlets were insufficient to allow characterization of bioaccumulation in the area.

Dyes and Sinclair Inlets are closed to commercial clamming and some beaches in both areas are posted with warning signs to discourage recreational clamming. Fish and clams are collected in the two inlets, however, and there is some concern that contaminants in fish and clams may pose a health threat. This study examined edible tissue in fish and clams collected in the waters near the Bremerton area.

The objectives of this study were to 1) determine concentrations of potentially toxic metals and organics in fish and clams in Sinclair Inlet and Dyes Inlet; 2) compare results to concentrations found elsewhere in Puget Sound and other locations cited in the literature; and 3) provide data for future assessment of potential public health risk. Samples were analyzed for PAHs, pesticides/PCBs, silver, arsenic, cadmium, chromium, copper, mercury, lead, zinc, and butyltins.

METHODS

Sample collections were made in two phases. The first phase collections were originally intended to be analyzed for all contaminants. These collections were made from September 2, 1989, to October 20, 1989. However, upon QA review, potential problems were seen in the PAH analysis. Thus, a second round of field work was conducted to collect samples for PAH. To verify earlier Phase 1 findings of no detectable pesticides/PCBs, these compounds were also examined in this second phase of sampling. This Phase 2 collection was made between September 20, 1990, and January 15, 1991. Phase 1 results reported here are for metals and butyltins. Phase 2 results reported are from PAH and pesticides/PCBs analysis. It is important to note that although sites were similar between sampling phases, the actual samples analyzed for metals and organics were different.

Locations

Figure 1 shows sample collection sites within Sinclair Inlet for this study. Figure 2 shows sites in Dyes Inlet. Table 1 shows the sampling dates, number of individuals collected, and location of samples. These sites were chosen in conference with the Bremerton-Kitsap County Health District, Northwest Regional Office of the Department of Ecology, Washington State Department of Health, and the Sinclair-Dyes Inlet Technical Working Group chaired by Department of Ecology to both reflect areas of recreational use and potential areas of contamination. Sites excluded from this study were those that had no apparent current harvest or that were posted and closed to recreational clam harvest. All clam sites provided a reasonable opportunity for recreational harvesters to collect clams. Sites 1, 5, 6, 7, and 8 are located near boat launches. The rest are near public access areas.

Fish collection sites were selected on the following rationale: Sites 7 and 8 are near boat launches and are both sites of recreational fishing. The Annapolis WWTP outfall is near Site 8. Site 7 is near the town of Port Orchard and the site of the abandoned outfall used by the Port Orchard WWTP. Site 10 is near the downtown Bremerton waterfront, the location of a ferry landing as well as a newly constructed marina and overwater park near 1st street. Site 11 is near a fishing pier. Most waterborne contaminants released into the water in Dyes Inlet will flow through Port Washington Narrows (Site 12), the only exit out of Dyes Inlet. No fish or clams were collected directly off of the Puget Sound Naval Shipyard because the areas adjacent to the shipyard are already closed to recreational clam gathering and vessel operation.

During Phase 1 sampling, clams were collected at eight sites throughout Sinclair and Dyes Inlets. Fish were collected at five sites in Sinclair Inlet and Port Washington Narrows. Clams collected were primarily Native littleneck clams (*Protothaca staminea*) and Japanese littleneck clams (*Tapes japonica*). Fish collected were five varieties of sole: Sand sole (*Psettichthys melanostictus*), English sole (*Parophrys vetulus*), C-O sole (*Pleuronichthys coenosus*), Rock sole (*Lepidopsetta bilineata*), and Flathead sole (*Hippoglossoides elassodon*). Sole were selected

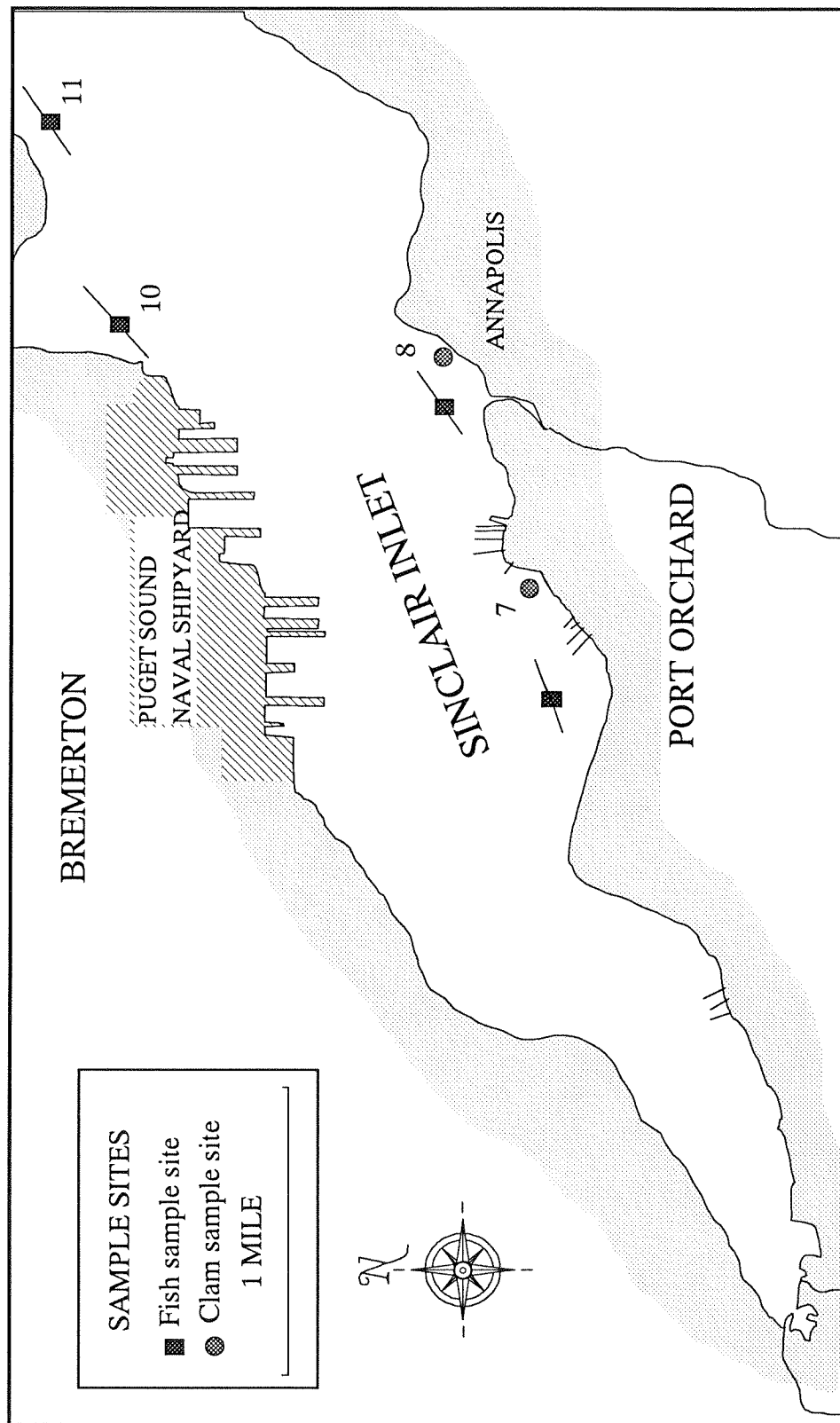


Figure 1. Sample sites in Sinclair Inlet

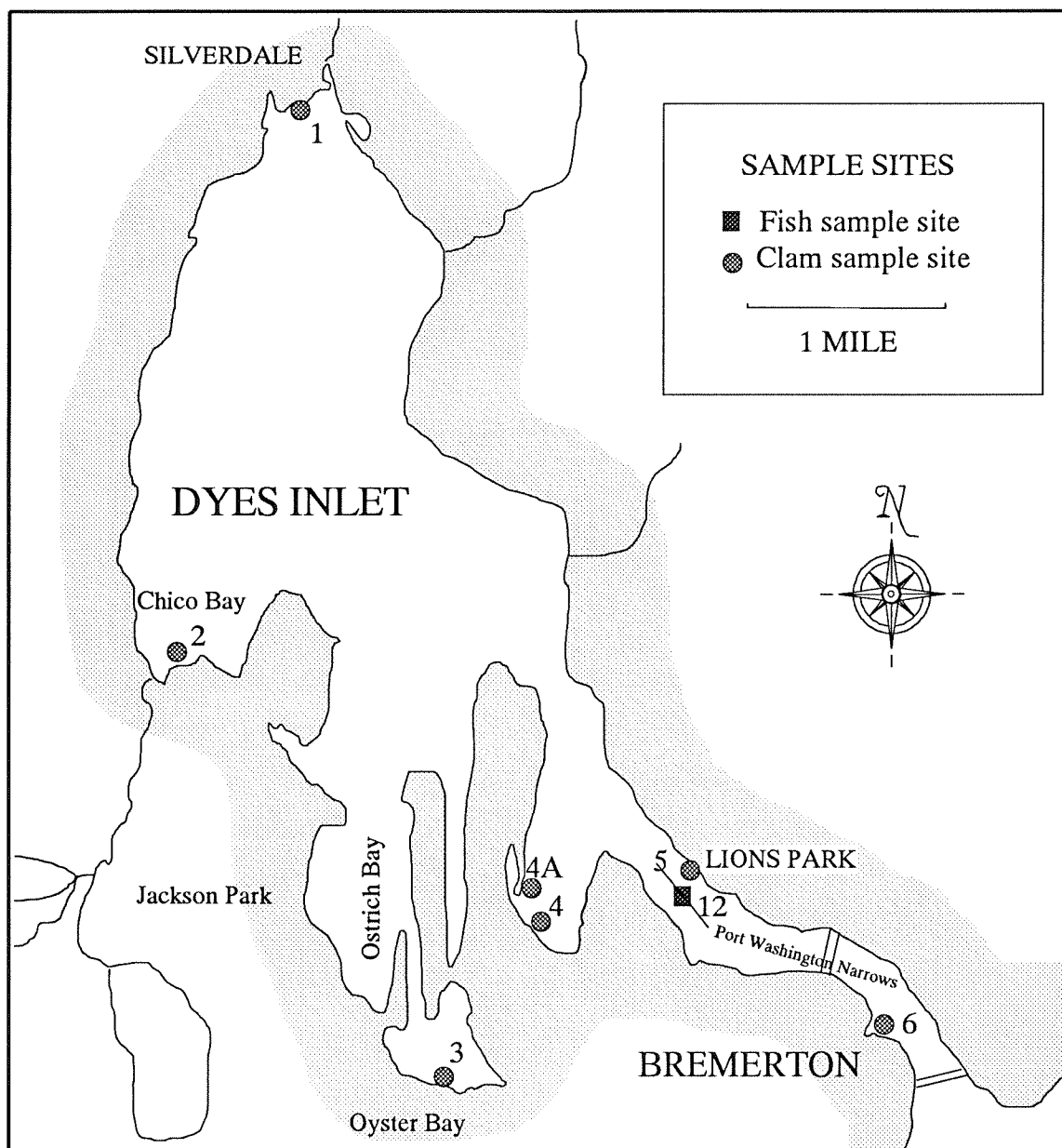


Figure 2. Sample sites in Dyes Inlet

Table 1. Samples collected in Sinclair and Dyes Inlets for analysis.

Table 1. Samples collected in Chinook and Dyes Rivers for analysis.

Date	Site	Number	Species	Average	Position		Description
Collected		Sampled	Composition	Length cm	Latitude	Longitude	
Fish		Phase 1: Metals and Butyltins					
10/19/89	7	4	3 SS, 1 ES	28.3	47° 32.5'	122° 38.6'	Port Orchard
10/19/89	8	6	3 COS, 3 RS	28.6	47° 32.6'	122° 37.6'	Annapolis
10/20/89	10	4	2 COS, 2 RS	27.6	47° 35.6'	122° 37.6'	Bremerton 6th ST.
10/20/89	11	4	4 RS	27.3	47° 34.6'	122° 35.6'	Mannette Fish Dock
10/19/89	12	4	3 COS, 1 RS	27.7	47° 35.0'	122° 38.0'	Pt Washington Narrows
Clams							
09/02/89	1	23	23 JL	5.1	47° 38.6'	122° 41.7'	Silverdale
09/02/89	2	39	39 NL	4.8	47° 36.6'	122° 42.7'	Chico Bay
09/02/89	3	24	24 JL	4.8	47° 34.6'	122° 40.7'	Oyster Bay
09/02/89	4	24	24 NL	4.7	47° 35.6'	122° 39.6'	Phinney Bay
09/02/89	5	20	20 NL	5.3	47° 35.6'	122° 38.6'	Lions Park
09/02/89	6	6	6 BC	8.5	47° 34.5'	122° 37.6'	Evergreen Park
09/02/89	7	20	20 NL	4.6	47° 32.5'	122° 38.6'	Port Orchard
09/02/89	8	25	21 NL, 4 JL	4.5	47° 32.0'	122° 37.0'	Annapolis
Fish		Phase 2: PAH and chlorinated organics					
09/21/90	7	4	4 FS	30.1	47° 32.5'	122° 38.6'	Port Orchard
09/20/90	8	5	5 FS	32.4	47° 32.6'	122° 37.6'	Annapolis
09/20/90	12	5	5 RS	28.7	47° 35.6'	122° 37.6'	Pt Washington Narrows
09/21/90	10	5	5 RS	28.3	47° 34.6'	122° 35.6'	Bremerton 6th ST.
09/21/90	11	5	5 COS	26.8	47° 35.0'	122° 38.0'	Mannette Fish Dock
Clams							
01/15/91	3	29	28 JL, 1 NL	4.4	47° 34.6'	122° 40.7'	Oyster Bay
01/15/91	4A	26	22 NL, 4 JL	4.9	47° 35.6'	122° 39.6'	Phinney Bay
01/15/91	6	9	4 NL, 3 BC, 2 HC		47° 34.5'	122° 37.6'	Evergreen Park
12/13/90	7	23	23 NL	4.3	47° 32.5'	122° 38.6'	Port Orchard
12/13/90	8	26	25 NL, 1JL	4.2	47° 32.0'	122° 37.0'	Annapolis
Species							
SS: Sand sole		<i>Psettichthys melanostictus</i>					
ES: English sole		<i>Parophrys vetulus</i>					
COS: C-O sole		<i>Pleuronichthys coenosus</i>					
RS: Rock sole		<i>Lepidopsetta bilineata</i>					
FS: Flathead sole		<i>Hippoglossoides elassodon</i>					
JL: Japanese littleneck		<i>Tapes japonica</i>					
NL: Native littleneck		<i>Protothaca staminea</i>					
BC: Butter clam		<i>Saxidomus giganteus</i>					
HC: Heart cockle		<i>Clinocardium nuttali</i>					

based on ease of collection, close proximity to sediment, and comparison with other studies. During Phase 2, clams were collected at five sites (3, 4A, 6, 7, and 8) and fish were collected at five sites.

Collection Methods

Clams

Clams were collected with shovels and rakes at low tide. Employees of the Bremerton-Kitsap County Health District helped collect clams during Phase 1. All fish samples and all Phase 2 clams were collected by the Department of Ecology. Clams were sampled from at least two areas at least 20 meters apart. A sample of at least 20 clams was collected, rinsed with site water, placed in plastic five gallon buckets or one gallon paper buckets, and wrapped in aluminum foil and frozen whole at the earliest opportunity (within 12 hours). The clams were not allowed to depurate in order to provide a potential worst case exposure to recreational users who may ingest residual sediment held in the clams.

Fish

Fish were collected with a 3 meter otter trawl towed behind a Boston Whaler outfitted with an "A" frame and hydraulic winch. The trawl was operated with enough scope to assure the mouth of the net was riding on the bottom. Tows were conducted at 1-3 knots for five minutes from 2-6 times at each sampling site depending upon the catch. Samples from the net were unloaded into a clean 40 gallon plastic barrel and sorted. Fish taken for analysis were killed with a blow to the head, wrapped separately in aluminum foil, chilled on ice, and frozen within 12 hours. Trawling continued until at least 4 fish longer than 20 cm were collected of no more than two species total.

Sample Preparation

Fork length of fish and longest length of clam shells were measured. Samples from each site were prepared separately to avoid cross-contamination between sites. All stainless steel dissecting tools (forceps, scalpel, and knives) and blenders were decontaminated with the following procedure:

- 1) Wash in hot water and Liquinox® detergent;
- 2) rinse in tap water;
- 3) rinse in 10% nitric acid;
- 4) rinse with deionized water;
- 5) rinse with pesticide analysis grade acetone; and
- 6) air dry.

All tools were decontaminated between sites. Entire soft parts of clams and associated liquid were scooped out of shells directly into a glass blender with stainless steel blades. Fish were fileted while partially frozen on a glass plate or lab bench covered with aluminum foil. For fish samples, care was taken not to include viscera in the samples. Skin was discarded. After

homogenization, sample aliquots were poured into separate pollutant-free jars for the different component analyses. In some cases, different species were pooled for each site (see Table 1) to provide adequate amounts of tissue for analysis.

Sample Analysis

Samples were analyzed for percent solids, percent lipids, metals, PCBs, chlorinated pesticides, PAHs, and butyltins. Table 2 presents sample analysis methods. Analyses followed standard methods with the following exceptions:

- 1) For metals analyses, tissues were digested with nitric acid and hydrogen peroxide. The Puget Sound Protocols (PSEP, 1986) call for digestion with nitric and perchloric acid, but they also allow nitric acid/peroxide digestion. The peroxide digestion has produced acceptable recoveries in other studies.
- 2) Tissues for PAH analysis were extracted with a 50:50 mixture of methylene chloride and acetone using the Department of Ecology/EPA Manchester modification of the EPA Contract Laboratory Program (CLP) and method 8270 procedures. Since PAHs were the primary target analytes and low detection limits were desired, samples were cleaned up using gel permeation chromatography (GPC) at both 2000 and 1000 molecular weight cutoffs (method 3640) followed by silica gel cleanup method 3630. The extraction was optimized for low detection limits for PAH and thus the phenols and other semivolatile compounds usually searched for in this procedure were not found.
- 3) Butyltin samples were analyzed following the Puget Sound Estuary Program guidelines (EPA, 1989) which are based on Muller (1987) and Krone *et al.* (1989). Samples are extracted with tropolone and methylene chloride, cleaned up with Florisil® and measured with gas chromatograph with a flame photometric detector.

Laboratory Quality Assurance

Several tests were used to assess laboratory accuracy and precision. Overall, the data are usable though some data had to be qualified due to quality control variances (see Appendix for a quality assurance review).

RESULTS

Metals

Table 3 reviews concentrations of metals found in fish and clams. Due to quality control problems, arsenic, cadmium, and lead were reanalyzed (see Appendix for details). Values from

Table 2. Analytical methods for Sinclair and Dyes Inlets investigation.

Analysis	Method	Reference	Laboratory
As	Graphite Furnace Atomic Absorption	EPA 1986a	ARI Seattle
Cd	Graphite Furnace Atomic Absorption	EPA 1986a	ARI Seattle
Cr	Graphite Furnace Atomic Absorption	EPA 1986a	ARI Seattle
Cu	Inductively Coupled Argon Plasma	EPA 1986a	ARI Seattle
Hg	Cold Vapor Atomic Absorption	EPA 1986a	ARI Seattle
Pb	Graphite Furnace Atomic Absorption	EPA 1986a	ARI Seattle
Ag	Graphite Furnace Atomic Absorption	EPA 1986a	ARI Seattle
Zn	Inductively Coupled Argon Plasma	EPA 1986a	ARI Seattle
Base Neutral Acids (Optimized for PAH)	GC/MS method 8270	EPA 1986a	Ecology/EPA (Manchester Lab.)
Pest/PCB	GC/EC method 8080	EPA 1986a	Ecology/EPA (Manchester Lab.)
Butyltins	GC/EC method	EPA 1989	Ecology/EPA (Manchester Lab.)
% Moisture	Dry @ 105 degrees C	APHA 1985	Ecology/EPA (Manchester Lab.)
% Lipids	Gravimetric	EPA 1980	Ecology/EPA (Manchester Lab.)

Table 3. Metals concentrations in fish and clams from Sinclair and Dyes Inlets (mg/kg wet weight).

Fish						Clams							
Lab Num.	438090	438091	438092	438093	438094	438080	438081	438082	438083	438084	438085	438086	438087
Site Num.	7	8	10	11	12	1	2	3	4	5	6	7	8
Ag	0.017	0.027	0.008 U	0.008	0.014	0.64	0.36	0.61	0.05	0.33	0.59	0.15	0.28
As*	3.3 E	8.6 E	7.1 E	21.1 E	3.5 E	3.1 E	2.6 E	2.2 E	2.3 E	2.3 E	3.5 E	3.4 E	1.2 E
Cd*	0.008 U	0.008 U	0.008 U	0.008 U	0.008 U	0.25	0.28	0.22	0.28	0.29	0.08	0.32	0.25
Cr	0.24 E	0.05 E	2.2 E	0.29 E	0.06 E	4.5 E	0.11 E	0.13 E	0.12 E	0.09 E	1.29 E	0.3 E	0.17 E
Cu	2.0	0.47	0.77	0.31	0.66	2.0	1.2	4.8	0.87	1.7	19.8	1.8	3.7
Hg	0.07	0.39	0.26	0.10	0.33	0.03	0.02	0.03	0.03	0.02	0.03	0.03	0.04
Pb*	0.36 E	4.6 E	1.2 E	0.90 E	0.44 E	0.50 E	0.16 E	0.79 E	0.27 E	0.29 E	1.09 E	0.47 E	0.42 E
Zn	6.5	8.6	8.7	5.4	4.1	11.3	13.0	17.1	15.7	11.9	25.1	10.9	13.9
Initial Analysis													
As	2.8 E	10.2 E	8.2 E	22.0 E	3.3 E	3.5 E	2.0 E	1.7 E	1.7 E	2.2 E	3.5 E	3.8 E	0.8 E
Cd	0.008 U	0.008 U	0.008 U	0.008 U	0.008 U	0.22	0.21	0.19	0.20	0.28	0.063	0.27	0.22
Pb	0.39 E	4.7 E	1.33 E	0.86 E	0.15 E	0.44 E	0.18 E	0.53 E	0.21 E	0.22 E	0.98 E	0.64 E	0.34 E
Reanalysis (conducted due to quality control variance - see Appendix)													
As	3.8 E	6.9 E	6 E	20.2 E	3.7 E	2.7 E	3.2 E	2.6 E	2.9 E	2.3 E	3.4 E	3.0 E	1.7 E
Cd	0.020 U	0.02 U	0.019 U	0.019 U	0.038 U	0.28	0.35	0.25	0.35	0.30	0.09	0.37	0.28
Pb	0.34 E	4.4 E	1.1 E	0.93 E	0.72 E	0.56 E	0.13 E	1.1 E	0.33 E	0.36 E	1.2 E	0.29 E	0.49 E

*= Average of two analyses (Initial and reanalysis)

U= No contaminant detected at detection limit shown

E= Quantity is estimated due quality control problems (see Appendix for details).

these two analyses were averaged. Little geographic pattern is apparent for metals concentrations in fish or clams. Fish had higher concentrations of arsenic, lead, and mercury than clams. The highest concentrations of these metals in fish were: arsenic, 21.1 mg/kg; lead, 4.5 mg/kg; and mercury, 0.39 mg/kg (all wet weight basis). Clams had the highest concentrations of cadmium, silver, copper, and zinc. The highest concentrations of these metals were: cadmium, 25 mg/kg; silver, 0.64 mg/kg; copper, 19.8 mg/kg; and zinc, 25.1 mg/kg (all wet weight basis).

In fish, Site 8 near the Annapolis WWTP outfall ranked highest in mercury and lead, and second highest in arsenic behind Site 11 fish. To examine potential patterns, a ranking index was applied to the concentrations of arsenic, lead, and mercury, the three contaminants that were highest in fish. The five fish sites were ranked in decreasing order of levels of these three metals and the ranks were summed. Thus, if a site were highest in all three metals, its index would be 3. Site 8 had the highest rank index (4). Sites 10 and 11 both were next with indices of 8. These three sites are closest to the confluence of the Port Washington Narrows and Sinclair Inlet.

Pesticides/PCBs

In Phase 1, no pesticides/PCBs were found above quantitation limits in any samples. Table 4 presents results of pesticides/PCBs analysis during Phase 2. With the exception of DDE reported in fish from Site 7 at 1.8 $\mu\text{g/kg}$ (wet weight), no pesticide/PCBs were found in fish or clams in this study. Quantitation limits for PCBs were high. PCBs at concentrations below 20 $\mu\text{g/kg}$ for either Aroclor 1254 and Aroclor 1260 would not have been detected (see Discussion Section).

Polycyclic Aromatic Hydrocarbons

No PAH were found in fish above the quantitation limits shown in Table 5. PAHs were found in clams at moderate concentrations as shown in Table 6. The highest concentrations were found in clams from Site 7 and Site 3 (Port Orchard, 46 $\mu\text{g/kg}$ total PAH wet weight; Oyster Bay, 45 $\mu\text{g/kg}$ total PAH wet weight). The lowest were found in the composite sample from Site 6 (Evergreen Park: 11 $\mu\text{g/kg}$ total PAH wet weight). The three and four ring PAHs predominated in all samples where PAHs were found.

Butyltins

Table 6 shows results of analysis for butyltins. Very small amounts of dibutyltin were found in fish from Sites 8, 10, and 11. Tributyltin was found in fish from Site 7 and 11. In clams, tributyltins were found at all three sites tested (Sites 3,7,8). Trace amounts of dibutyltin and monobutyltin were also found in clams. The highest total of butyltins were found in clams at Site 7 (18.2 $\mu\text{g/kg}$ wet weight, at Port Orchard).

Table 4. Chlorinated hydrocarbons concentrations in fish and clams from Sinclair and Dyes Inlets (ug/kg wet wt.).

Pesticides	Fish							Clams				
	Lab Number	8205	8206	8207	8208	8209	8210	8211	8212	8213	8214	
	Site Number	7	8	10	11	12	3	4A	6	7	8	
Aldrin		2 U	2 U	1.9 U	1.9 U	2 U	2 U	2 U	2 U	2 U	2 U	
Chlordane		20 U	20 U	19 U	19 U	20 U	40 U	20 U	20 U	20 U	20 U	
Dieldrin		2 U	2 U	1.9 U	1.9 U	2 U	2 U	2 U	2 U	2 U	2 U	
4,4'-DDT		2 U	2 U	1.9 U	1.9 U	2 U	2 U	2 U	2 U	2 U	2 U	
4,4'-DDE		1.8 NJ	2 U	1.9 U	1.9 U	2 U	2 U	2 U	2 U	2 U	2 U	
4,4'-DDD		2 U	2 U	1.9 U	1.9 U	2 U	2 U	2 U	2 U	2 U	2 U	
alpha Endosulfan		2 U	2 U	1.9 U	1.9 U	2 U	2 U	2 U	2 U	2 U	2 U	
beta Endosulfan		2 U	2 U	1.9 U	1.9 U	2 U	2 U	2 U	2 U	2 U	2 U	
Endosulfan sulfate		2 U	2 U	1.9 U	1.9 U	2 U	2 U	2 U	2 U	2 U	2 U	
Endrin		2 U	2 U	1.9 U	1.9 U	2 U	2 U	2 U	2 U	2 U	2 U	
Endrin aldehyde		2 U	2 U	1.9 U	1.9 U	2 U	2 U	2 U	2 U	2 U	2 U	
Heptachlor		2 U	2 U	1.9 U	1.9 U	2 U	2 U	2 U	2 U	2 U	2 U	
Heptachlor epoxide		2 U	2 U	1.9 U	1.9 U	2 U	2 U	2 U	2 U	2 U	2 U	
alpha-BHC		2 U	2 U	1.9 U	1.9 U	2 U	2 U	2 U	2 U	2 U	2 U	
beta-BHC		2 U	2 U	1.9 U	1.9 U	2 U	2 U	2 U	2 U	2 U	2 U	
gamma-BHC		2 U	2 U	1.9 U	1.9 U	2 U	2 U	2 U	2 U	2 U	2 U	
delta-BHC		2 U	2 U	1.9 U	1.9 U	2 U	2 U	2 U	2 U	2 U	2 U	
Toxaphene		120 U	120 U	120 U	120 U	120 U	120 U	120 U	120 U	120 U	120 U	
Methoxychlor		2 U	2 U	1.9 U	1.9 U	2 U	2 U	2 U	2 U	2 U	2 U	
PCBs												
Aroclor-1016		20 U	20 U	19 U	19 U	20 U	20 U	20 U	20 U	20 U	20 U	
Aroclor-1221		20 U	20 U	19 U	19 U	20 U	20 U	20 U	20 U	20 U	20 U	
Aroclor-1232		20 U	20 U	19 U	19 U	20 U	20 U	20 U	20 U	20 U	20 U	
Aroclor-1242		20 U	20 U	19 U	19 U	20 U	20 U	20 U	20 U	20 U	20 U	
Aroclor-1248		20 U	20 U	19 U	19 U	20 U	20 U	20 U	20 U	20 U	20 U	
Aroclor-1254		20 U	20 U	19 U	19 U	20 U	20 U	20 U	20 U	20 U	20 U	
Aroclor-1260		20 U	20 U	19 U	19 U	20 U	20 U	20 U	20 U	20 U	20 U	
Percent lipid		0.1%	0.1%	0.2%	0.0%	0.2%	0.2%	0.2%	0.4%	0.3%	0.2%	
Percent solids		18.4%	16.7%	18.0%	19.3%	21.0%	12.1%	11.2%	11.8%	12.0%	11.8%	

U = No pesticide found at detection limit shown

J = Estimated quantity due to low signal to noise ratio

N = Presumptive evidence of presence

Table 5. PAH concentrations in fish and clams from in Sinclair and Dyes Inlets (ug/kg wet weight).

Lab Number	Fish							Clams				
	8205	8206	8207	8208	8209	8210	8211	8212	8213	8214		
Site	7	8	10	11	12	3	4A	6	7	8		
Naphthalene	97 U	96 U	91 U	93 U	95 U	96 U	96 U	95 U	96 U	95 U		
2-Methylnaphthalene	97 U	96 U	91 U	93 U	95 U	96 U	1 J	95 U	96 U	0.8 J		
Acenaphthylene	97 U	96 U	91 U	93 U	95 U	96 U	96 U	95 U	96 U	95 U		
Acenaphthene	97 U	96 U	91 U	93 U	95 U	96 U	96 U	95 U	96 U	95 U		
Fluorene	97 U	96 U	91 U	93 U	95 U	96 U	96 U	95 U	96 U	95 U		
Phenanthrene	97 U	96 U	91 U	93 U	95 U	7 J	5 J	7 J	8 J	4 J		
Anthracene	97 U	96 U	91 U	93 U	95 U	96 U	96 U	95 U	96 U	95 U		
Sum LPAH						7 J	6 J	7 J	8 J	5 J		
Fluoranthene	97 U	96 U	91 U	93 U	95 U	16 J	7 J	95 U	20 J	12 J		
Pyrene	97 U	96 U	91 U	93 U	95 U	18 J	6 J	95 U	18 J	10 J		
Benzo(a)anthracene	97 U	96 U	91 U	93 U	95 U	96 U	96 U	95 U	96 U	95 U		
Chrysene	97 U	96 U	91 U	93 U	95 U	96 U	96 U	95 U	96 U	95 U		
Benzo(b)fluoranthene	97 U	96 U	91 U	93 U	95 U	4 J	96 U	4 J	96 U	95 U		
Benzo(k)fluoranthene	97 U	96 U	91 U	93 U	95 U	96 U	96 U	95 U	96 U	95 U		
Benzo(a)pyrene	97 U	96 U	91 U	93 U	95 U	96 U	96 U	95 U	96 U	95 U		
Indeno(1,2,3-cd)pyrene	97 U	96 U	91 U	93 U	95 U	96 U	96 U	95 U	96 U	95 U		
Dibenzo(a,h)anthracene	250 U	240 U	230 U	240 U	240 U	240 U	240 U	240 U	240 U	240 U		
Benzo(ghi)perylene	97 U	96 U	91 U	93 U	95 U	96 U	96 U	95 U	96 U	95 U		
Sum HPAH						38 J	13 J	4 J	38 J	22 J		

U = Limit of quantitation

J = Estimate due to low signal to noise ratio

Table 6. Butlytin concentrations in fish and clams from Sinclair and Dyes Inlets (ug/kg wet weight).

Lab Number	Fish				Clams		
Site	8090	8091	8092	8093	8082	8086	8087
	7	8	10	11	3	7	8
Tetrabutyltin	6.0 U	5.8 U	6.0 U	5.9 U	5.8 U	5.7 U	5.5 U
Tributyltin	3.5 NJ	5.4 U	5.6 U	2.0 NJ	14.5	13.1	1.7 NJ
Dibutyltin	5.2 U	1.0 NJ	1.4 NJ	0.7 NJ	2.7 NJ	4.2	4.8 U
Monobutyltin	4.8 U	4.7 U	4.8 U	4.7 U	4.6 U	0.91 NJ	4.4 U

U = Limit of quantitation

N = Presumptive evidence of presence

J = Estimate due to low signal to noise ratio

DISCUSSION

Fish species and, to some extent, clam species varied by site. For some samples, species were pooled. Because of this variation, whether genuine differences in concentrations occurred between sites, between species, or merely between samples, cannot be isolated. These analyses of fish and shellfish do provide a guideline or indication of concentrations to which consumers of fish and shellfish collected in the Sinclair and Dyes Inlets area may be exposed.

Comparison to Other Studies - Fish

Metals

Table 7 compares concentrations of metals found in this study to other studies that examined fish muscle in Puget Sound. Chromium, copper, lead, and mercury all were higher in this study than in comparable studies in Puget Sound urban bays. Most noteworthy are the relatively high concentrations of mercury compared to other studies in Sinclair Inlet and other urban bays. These high concentrations of mercury are consistent with other studies of sediment. Of 34 stations sampled throughout Puget Sound, Sinclair and Dyes Inlets had the highest concentrations of mercury in sediments (Striplin *et al.*, 1991). Most all concentrations of metals found in this study exceed metals levels found in previous studies of Sinclair Inlet fish muscle. Due to differences in species and methods between studies, conclusions about temporal trends cannot be made.

Crecelius *et al.* (1989) examined fish from 13 bays in Puget Sound and found little variation between sites in the concentrations of metals. The one exception in that study was arsenic. Higher concentrations of arsenic were found in sites near an historic source of arsenic, the ASARCO smelter in Tacoma. If the samples in Table 7 collected near this source at Point Defiance are excluded from consideration, the arsenic concentrations in the present study average nearly twice the concentrations in other areas of Puget Sound. Note that earlier studies in Sinclair Inlet found arsenic in fish muscle at approximately the same concentrations as the reference area in Discovery Bay. Again, these higher concentrations found in this study are without clear explanation, however, because of limitations in the comparability of the data, they cannot denote a temporal trend.

Pesticides

No pesticides were found in any tissues in this study with the one exception of DDE in fish at Site 7. Table 8 reviews concentrations of pesticides/PCBs found in fish in other studies in Puget Sound. The detection limits reported in this study are consistently higher than the results of other studies. In the case of DDT and its metabolites, DDE and DDD, concentrations found in other studies are higher than the detection limits reported in this study.

Table 7. Comparison of metals concentrations in fish muscle reported by other studies in Puget Sound (mg/kg wet weight).

Location	Species	N	As	Cd	Cr	Cu	Pb	Hg	Ag	Zn	Study
<u>Urban Areas</u>											
Pt Defiance Dock	C-O Sole	1	38	0.00 U	0.18	0.44	0.65	0.02	0.006 U	10.7	Gahler et al. 1982
Pt Defiance Dock	English Sole	3	8.6	0.00 U	0.28	0.39	3.9	0.03	0.006 U	6.5	"
Pt Defiance Dock	Rock sole	3	16	0.00	0.24	0.41	0.48	0.05	0.006 U	9.1	"
City Waterway	Flathead sole	1	1.0	0.00 U	0.47	0.25	0.35	0.04	0.007 U	4.3	"
City Waterway	English sole	5	5.1	0.00 U	0.31	0.32	0.32	0.04	0.01 U	5.5	"
Elliott Bay	Sole	6	7.4	-	0.05	0.53	0.03	0.08	0.003	5.4	Romberg et al 1984
Liberty Bay	Rock sole	1	4.5	0.030	0.09	0.15	0.14	0.08	0.000	4.4	Crecelius et al. 1989
Pt. Townsend	Rock sole	1	3.1	0.030	0.08	0.22	0.18	0.004	0.0008	3.6	"
		Min	1.0	0.005 U	0.05	0.15	0.03	0.00	0.0008	3.6	
		Max	38	0.030	0.47	0.53	3.9	0.08	0.003	10.7	
		Median	6.2	0.007 U	0.20	0.36	0.33	0.04	0.007 U	5.5	
<u>Sinclair and Dyes Inlets</u>											
Sinclair Inlet	Starry flounder	1	1.7	0.01	-	0.27	0.002	0.011	0.0005 U	4.5	Landolt et al. 1987
Sinclair Inlet	Starry flounder	1	2.2	0.00	-	0.40	0.002	0.014	0.0005 U	6.6	"
Sinclair Inlet	Starry flounder	1	1.8	0.00	-	0.24	0.002	0.017	0.001	5.2	"
Sinclair Inlet	Starry flounder	1	1.2	0.00	-	0.22	0.002	0.002 U	0.0005	3.9	"
Sinclair Inlet	English Sole	1	6.1	0.03	0.16	0.27	0.50	0.079	0.0071	3.3	Crecelius et al. 1989
Dyes Inlet	English Sole	1	5.7	0.03	0.20	0.22	0.33	0.004	0.0013	2.4	"
		Min	1.2	0.003	0.16	0.22	0.002	0.002 U	0.0005	2.4	
		Max	6.1	0.038	0.20	0.40	0.50	0.079	0.0071	6.6	
		Median	2.0	0.008	0.18	0.25	0.002	0.012	0.0007	4.2	
Sinclair Inlet		Min	3.3 E	0.008 U	0.05	0.31	0.36 E	0.07	0.01	4.1	This study
		Max	21 E	0.008 U	2.2	2.0	4.6 E	0.39	0.03	8.7	"
		Median	8.6 E	0.008 U	0.24	0.66	0.90 E	0.26	0.01	6.6	"
<u>Reference Area</u>											
Discovery Bay	Flathead sole	1	5.3	0.00 U	0.07	0.28	0.31	0.04	0.01 U	4	Gahler et al. 1982
	English Sole	5	3.2	0.00 U	0.06	0.42	0.46	0.04	0.01 U	5.2	"

U = No contaminant found at detection limit shown.

Table 8. Comparison of chlorinated hydrocarbon concentrations in fish muscle reported by other studies in Puget Sound.
(All values ug/kg wet weight.)

Location	Species	N	HCB	DDE	DDD	DDT	Sum PCBs	G-BHC	Heptachlor	Aldrin	Chlordane	Dieldrin	Study
<u>Urban Bays</u>													
Pt Defiance Dock	C-O Sole	1	1 U	1	1 U	1 U	1 U	70	-	-	-	-	Gahler et al. 1982
Pt Defiance Dock	English Sole	3	1.0 U	3	4	2	330	-	-	-	-	-	"
Pt Defiance Dock	Rock sole	2	1 U	26	1	4	120	-	-	-	-	-	"
City Waterway	Flathead sole	1	1.0 U	1	1 U	1 U	33	-	-	-	-	-	"
City Waterway	English Sole	5	1.0 U	5	8	4	190	-	-	-	-	-	"
Elliott Bay	Sole	6	0.0 N	2.3	ND	ND	166	ND	ND	-	-	ND	Romberg et al 1984
Liberty Bay	Rock sole	1	0.6	0.7	1.0	0.1	55	0.9 U	0.1 U	1.0 U	0.2	0.3	Creceilius et al. 1989
Pt. Townsend	Rock sole	1	1.0	0.5	1.0	0.1 U	53	1 U	0.2 U	2.0 U	0.5	0.4	"
	Min			0.5	1.0	0.10	33	-	-	-	-	-	
	Max			26	8	4.00	330	-	-	-	-	-	
	Avg			5.2	2.9	1.8	169	-	-	-	-	-	
<u>Sinclair and Dyes Inlets</u>													
Sinclair Inlet	Starry Flounder	1		8.0	ND	2.1	108	-	-	-	-	-	Landolt et al. 1987
Sinclair Inlet	Starry Flounder	1		2.8	0.8	ND	345	-	-	-	-	-	"
Sinclair Inlet	Starry Flounder	1		6.2	ND	2.1	227	-	-	-	-	-	"
Sinclair Inlet	Starry Flounder	1		15.6	119	2.1	196	-	-	-	-	-	"
Sinclair Inlet	Starry Flounder	1		2.4	ND	ND	64	-	-	-	-	-	"
Dyes Inlet	English Sole	1	0.8	0.7	2.0	0.3	97	1 U	0.1 U	1.0 U	0.6	0.6	Creceilius et al. 1989
Sinclair Inlet	English Sole	1	0.9	1.0	2.0	0.4	137	0.8 U	0.1 U	1.0 U	0.8	0.9	"
	Min		0.8	0.7	0.8	0.3	64	-	-	-	-	-	
	Max		0.9	15.	119	2.0	345	-	-	-	-	-	
	Min		2.0 U	1.8 NJ	2 U	2 U	40 U*	2 U	2 U	2 U	20 U	2 U	This study
	Max		2.0 U	1.8 NJ	2 U	2 U	40 U*	2 U	2 U	2 U	20 U	2 U	"
<u>Reference Area</u>													
Discovery Bay	Flathead sole	1	1 U	1	1 U	1 U	10 U	-	-	-	-	-	Gahler et al. 1982
	English Sole	5	1 U	3	1 U	1	13	-	-	-	-	-	"

U= No contaminant detected at detection limit shown

J= Concentration is estimate due to low signal to noise ratio

N= Presumptive evidence of chemical presence

* = Sum of detection limits for Arochlor 1260 and Arochlor 1254

ND= No contaminant detected and no detection limit provided.

A source of greater concern and perplexity is the lack of PCBs found in this study. All other studies listed have found PCBs in concentrations greater than the combined detection limits of Aroclor 1254 and Aroclor 1260 (the two most environmentally prevalent PCBs). In fact, PCBs were reported for all samples except the flathead sole collected in the reference area in Discovery Bay. Reference areas are presumed to have little contamination and used as a control in other studies. These pesticide/PCBs analyses are the second conducted in this study and they verify the results found in the initial survey. It is unlikely PCB concentrations in fish in Sinclair and Dyes Inlets have decreased substantially over the three years since the Crecelius *et al.* study. One possible explanation for the inability to detect PCBs is the low lipid weight reported in the samples. All the organochlorine contaminants are lipophilic and the concentrations would thus be proportional to the amount of lipids present in the tissues.

Polycyclic Aromatic Hydrocarbons

No PAHs were found in fish muscle tissue and few studies have reported PAH in fish muscle. Fluorescent aromatic hydrocarbons have been reported in fish bile (Krahn *et al.*, 1987) in English sole from Puget Sound, and these compounds indicate the presence of PAH. Crecelius *et al.* (1989), examining English sole bile from 9 sites found the highest concentrations of naphthalene in fish from Sinclair Inlet (44,000 $\mu\text{g/kg}$). Benzo(a)pyrene, a known carcinogenic PAH was also found in English sole bile from Sinclair Inlet at the second highest concentration encountered (420 $\mu\text{g/kg}$ wet weight). However, because the present study's focus was to examine contaminants in fish to which recreational fish consumers may be exposed, no fish bile or liver tissue was examined and this study shows little PAH is available to consumers of bottom fish muscle.

Butyltins

Tributyltin was found in fish at apparently very low concentrations in this study. Few data are available on butyltin concentrations in Puget Sound seafood. Short and Thrower (1986) examined salmon collected from public markets in Seattle and found measurable tributyltin in two of five samples (range: 81-200 $\mu\text{g/kg}$ wet weight). The source of the tributyltin was inferred to be antifouling paint applied to aquaculture pens. These concentrations are considerably higher (1 or 2 orders of magnitude) than found in this study. Short and Thrower (1986) also demonstrated bioaccumulation of tributyltin in salmon increases with time exposed.

Comparison to Other Studies - Clams

Metals

Table 9 compares concentrations of metals found in clams in this study to other studies in Puget Sound. Mean concentrations of the arsenic, cadmium, lead, and zinc examined in this study are

Table 9. Comparison of metals concentrations in clams with other studies in Puget Sound.
(All values mg/kg wet weight).

Metal	Non-Reference Area*				Reference Area**			
	Elliott Bay	Puget Sound	Eagle Harbor	McNeil Island	Birch Bay	Point Blakely	Horsehead Bay	Sinclair and Dyes Inlets
	5 sites	8 sites	1 site	1 site	1 site	1 site	1 site	8 sites
***Species code:	1	2	3	2	2	3	2	
Study:	Romberg et al. 1984	Faigenblum 1988	Yake et al. 1984	Norton 1988	Faigenblum 1988	Yake et al. 1984	Norton 1988	This study
As	Mean Range N	2.4 1.8-3.5 5	2.70 1.3-4.1 32	1.3 1.1-1.4 3	2.6 2.1-3.2 5	3.7 1	1.4 1	2.6 1.2-3.5 8
Cd	Mean Range N	0.13 .10-.19 5	0.16 .08-.29 8	0.31 .29-.34 3	0.3 .22-.36 6	0.11 1	0.35 1	0.25 .08-.32 8
Cr	Mean Range N	2.4 .51-5.7 5	0.51 .08-.8 8	<.1-.27 3		0.55 1	0.47 1	0.84 .09-4.5 8
Cu	Mean Range N	4 3.0-5.4 5	1.3 <.6-2.4 32	0.88 .68-.99 3	1 <.6-1.6 5		2.3 1	4.5 1.2-19.8 8
Pb	Mean Range N	0.40 .10-.50 5	0.09 .04-.18 25	0.84 .43-2.0 8	<.04- 4	0.38 1		0.5 .16-1.1 8
Hg	Mean Range N	0.020 .11-.28 5	0.02 <.02-.03 25	0.011 .010-.011 3	<.02- 3	0.012 1	0.012 1	0.028 .02-.04 8
Zn	Mean Range N	18 16-23 5	15.2 12-21 39	14.1 12-15 8	16 14-18 2	12 1	9.4 1	14.9 10.9-25.1 8

*Presumption within study that area may exceed background concentrations.

**Used within studies as reference or control site.

***Species codes:

1	2	3
<i>Saxidomus giganteus</i>	<i>Protothaca staminea</i>	<i>Protothaca staminea</i>
		<i>Saxidomus giganteus</i>
		<i>Tapes japonica</i>
		<i>Tresus capax</i>
		(first two predominated)

comparable to concentrations in clams from reference areas (areas presumed to have little contamination and used as a control in other studies). Mercury, chromium, and copper concentrations are equivalent to concentrations found in non-reference areas.

Pesticides/PCBs

The low concentrations of lipids found in the clams may contribute to the lack of pesticides and PCBs found in these tissues. Also, if quantitation limits had been lower, PCBs might have been found.

Polycyclic Aromatic Hydrocarbons

Table 10 shows PAH concentrations of found in clams at other sites in Puget Sound. The total PAH concentration in the clams from this study is comparatively low and equivalent to reference areas. LPAH concentrations in clams are below those found in smoked foods, but HPAH concentrations found in clams in the present study are equivalent to those found in smoked fish.

Butyltins

Few comparative data exist for butyltins in clams. Table 11 compares what data are available and shows comparatively low concentrations in this study. The highest concentrations of tributyltins were found at Sites 3 and 7. Both these sites are associated with marinas and thus with boat storage. Wade *et al.* (1988) compared concentrations of butyltins in oysters and mussels nationwide and found butyltins in Sinclair Inlet mussels were roughly 1/3 of the study average. Tributyltin in Sinclair Inlet water column was examined by Grovhoug *et al.* (1987). Of 15 sites examined, three showed measurable concentrations. Two of those sites were near Site 7 (Port Orchard Marina).

Comparisons to Standards

The U.S. FDA issues guidelines for contaminants in food called Action Levels (FDA, 1984; FDA, 1985). When these levels are exceeded, the product cannot be commercially traded. These concentrations are not based on risk assessment models and therefore do not account for variations in consumption levels.

The FDA limit for mercury is based on total methylmercury and is set at 1.0 mg/kg wet weight and represents a judgement by FDA to balance the potential risk of consumption against economic considerations. Some states (e.g., Wisconsin and California) have adopted 0.5 mg/kg wet weight as a guideline for health advisories in consumption of sport fish, based on potential adverse effects on pregnant women and their children, as well as on people who consume fish at a higher rate than assumed by the FDA (Wisconsin, Anderson and Olson, 1986; California, Stratton *et al.*, 1987). The FDA formerly had an action level of 0.5 mg/kg but raised it to 1.0 in 1979 (FDA, 1979). Johnson *et al.* (1988) suggest the FDA faces a regulatory problem at the 0.5 mg/kg level because some commercial species commonly exceed this concentration.

Table 10. Comparison of PAH concentrations in clams with other studies in Puget Sound. (All values ug/kg wet weight).

Chemical	Species code**** Study:	Non-Reference Area*			Reference Area**			Sinclair &		Selected Foods	
		Eagle	S. Budd	Industrial	Point	N. Budd	Case	Dyes Inlets	Smoked	Smoked	
		Harbor 1 Yake et al. 1984	Inlet 2 Norton 1986	Waterway*** 3 Malins et al 1980	Blakely 1 Yake et al. 1984	Inlet 2 Norton 1986	Inlet 3 Malins et al 1980	5 sites This study	Ham Pucknat 1981	Fish Pucknat 1981	
LPAH(1)											
	Mean	126	67	47	21	<10	<1	6.5			
	Range	14-690	16-159	6-96				5-8			9.2-145
	N	8	3	4	1	1	1	5			
HPAH(2)											
	Mean	403	373	386	76	<10	<1	23			
	Range	45-1575	72-938	138-701				4-38	10-496		3-30
	N	8	3	4	1	1	1	5			

*Presumption within study that area may exceed background concentrations.

**Used within study as reference or control site.

***Duwamish, Commencement Bay, and Hylebos Waterways, Seattle Waterfront

****Species codes:

	1	2	3
<i>Protothaca staminea</i>	<i>Protothaca staminea</i>	<i>Macoma nasuta</i>	
<i>Tapes japonica</i>	<i>Tapes japonica</i>	<i>Macoma carlottensis</i>	
<i>Saxidomus giganteus</i>	<i>Mya arenaria</i>	<i>Acila castrensis</i>	

(1)LPAH = Low molecular weight Polycyclic Aromatic Hydrocarbons. (2 and 3 ring compounds)

(2)HPAH = High molecular weight Polycyclic Aromatic Hydrocarbons. (4,5 and 6 ring compounds)

Table 11. Comparison of butyltin concentrations in clams from Sinclair and Dyes Inlets. (All values ug/kg wet weight).

	Sinclair Inlet	Sinclair and Dyes Inlets	
	Wade et al. 1988	This study	
	Mussels	Clams	N Detected/N
Tetrabutyltin		<5.5U	0/3
Tributyltin	150	1.7-14.5NJ	3/3
Dibutyltin	70	2.7-4.2NJ	2/3
Monobutyltin	50	0.91 NJ	1/3
	N	1	3

U = Limit of quantitation

N = Likely presence

J = Estimate due to low signal to noise ratio

In this study, no samples exceeded the 0.5 mg/kg concentration, although two fish samples approached this limit at concentrations between 0.3 and 0.4 mg/kg wet weight. The FDA issues no other limits for metals.

FDA action limits for organics include PCBs and several pesticides. The FDA limit for total PCBs at 2 mg/kg. The pesticide limits for DDE is 5 mg/kg and for chlordane it is 0.3 mg/kg. Concentrations in all samples were far below these limits.

Human Health Risk Review

To help assess human health risk in the consumption of fish and clams from Sinclair and Dyes Inlets, methods from Tetra Tech (1988b) were applied to contaminant data from this study. These assessments are rudimentary and only seek to estimate risks of cancer and toxicity. They do not evaluate teratogenic or mutagenic effects. Table 12 shows of results of health risk calculations.

Carcinogens

Arsenic is the only carcinogen found in this study at levels elevated enough to cause concern at a cancer risk of greater than 1×10^{-6} . PCBs, the source of greatest carcinogenic risk associated with fish consumption in Puget Sound (Tetra Tech, 1988b), were not detected in this study. No assumptions were made about the concentration of PCBs below the quantitation limits of these analyses.

Carcinogenic risk associated with arsenic in Sinclair Inlet fish was at the 10^{-5} level for consumption of 12 g/day (a proportionally high amount). Seafood tends to have high concentrations of arsenic. Tetra Tech (1988b) provides comparison data of carcinogenic risks based on work by Crouch and Wilson (1984), and Allman (1985). Carcinogenic risk of eating 100 charcoal broiled steaks per year is calculated at 7×10^{-5} level and eating four tablespoons of peanut butter/day provides a 6×10^{-4} level of cancer risk from aflatoxins. Cigarette smoking presents an 8×10^{-2} (.08) lifetime risk of cancer.

Non-carcinogens

A risk index of non-carcinogens are derived as a ratio of exposure dose to a reference dose. The reference dose is an estimated single daily chemical intake rate that appears to be without risk when ingested over a lifetime. Thus a risk index of greater than one indicates that lifetime exposure exceeds the level at which toxic effects may be observed. Concentrations of metals in Table 12 did not create risk indices greater than one. However, when the indices were added and provided cumulative risk indices, they approached one. The possibility exists that the cumulative risk index for the worst case (highest concentration in fish) could exceed one if: (1) more chemicals were examined and these chemicals had reference dose data; or (2) assumptions about dose are changed (more fish consumption, less body weight).

Table 12. Risk in consumption of fish and clams from Sinclair and Dyes Inlets.

Chemical	Concentration (mg/kg wet weight)			Carcinogen		Carcinogenic Risk*			
	Fish		Clams		Potency (mg/kg/day)-1	Fish		Clams	
	Median	Max	Median	Max		Median(1)	High(2)	Median	High
Arsenic	8.55	21.1	2.41	3.5	1.5	2E-05	5E-05	6E-07	8E-07
Reference dose									
(mg/kg/day)									
Cadmium			0.26	0.32	0.0003			0.014	0.017
Copper	0.66	2	1.89	19.8	0.037	0.003	0.009	0.001	0.008
Lead	0.9	4.55	0.45	1.1	0.0014	0.110	0.557	0.005	0.012
Mercury	0.02	0.39	0.03	0.04	0.0003	0.015	0.223	0.002	0.002

*Carcinogenic risk based on the following:

Consumption: fish=12g/d, clams=1.1g/day; exposure duration=70 yrs; body weight=70kg; absorption coefficient=0.01

Dose=(concentration X consumption X absorption)/body weight

Risk=1-exp(-dose X carcinogenic potency)

**Non-carcinogenic risk index based on the following:

Consumption: fish=12g/d, clams=1.1g/day; exposure duration=70 yrs; body weight=70kg; absorption coefficient=1.0

Dose=(concentration X consumption X absorption)/body weight

Risk index=dose/reference dose

Risk index <1 indicates acceptable level

(1)Median: Dose based on median concentration of composite samples.

(2)High: Dose based on highest concentration in any composite sample (max).

Methods and assumptions from Tetra Tech (1988b).

The methods used to derive these cumulative risk estimates must be regarded as tentative (Tetra Tech, 1988b). They may underestimate risk because all potentially hazardous chemicals have not been analyzed in any sample. These cumulative risk estimates cannot reconcile potential synergistic or antagonistic effects among non-carcinogens. Finally, these non-carcinogens can differ in their areas of physiological effects and thus their risks may not be additive.

CONCLUSIONS

Concentrations of several metals in fish from Sinclair and Dyes Inlets exceeded those found in comparable studies in the same area and were equivalent or higher than fish from other urban bays. Most importantly, mercury in fish in the present study (0.4 mg/kg) approached the FDA action limit of 1 mg/kg. The California limit is 0.5 mg/kg. Of great surprise was the complete lack of PCBs detected in fish tested, although two completely independent sample series were analyzed. Only one chlorinated hydrocarbon pesticide (DDE) was found in fish or clams. PAHs were found in clams at low concentrations. Butyltins were found in fish and clams at low concentrations.

Tentative and rudimentary risk assessments showed a small carcinogenic risk (10^{-5}) from habitual and ample consumption of seafood from the area. The non-carcinogenic risk of regular consumption of fish was low, but could be moderate in worst case situations.

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APPENDIX

APPENDIX: LABORATORY QUALITY ASSURANCE

Several tests were used to assess laboratory accuracy and precision. Overall, the data are usable with some qualification. Following are reviews of the quality assurance tests and laboratory reports.

Matrix Spike: Matrix spikes were performed for each of the three types of analyses. A known amount of the target compound was added to the matrix (homogenized tissue) and the recovery of the compound was a measure of extraction efficiency and analytical accuracy. Cadmium and lead both had inconsistent matrix spike recoveries.

Replicate Analysis: Relative percent difference (RPD) was calculated from results of replicate analyses as a measure precision. The formula for RPD is

$$RPD = (S1-S2)/((S1+S2)/2) * 100$$

where S1 and S2 are the duplicate samples. Matrix spike samples were analyzed in duplicate so that there were two RPD measurements. Duplicate analyses of metals showed some problems. The precision was problematic for arsenic, chromium, and lead. Upon reanalysis the precision improved.

Surrogate Recovery: For the gas chromatography analyses, recovery of surrogates added before extraction were analyzed. Surrogates have similar chemical structure to the analytes of interest but are not expected to be found in the environment. For the pesticides, three surrogates, 4,4 dibromooctafluorobiphenyl, dibutylchlorodate, and octochloronaphthalene were used. In the base, neutral, and acid extraction, due to the silica gel cleanup and optimization for PAHs, only the non-polar surrogates terphenyl-d14, pyrene-d10, and 2-fluorobiphenyl were recovered. Butyltin surrogate was tripropyltin. All surrogates recoveries were within EPA CLP guidelines for sediment (there are no CLP guidelines for tissues or butyltins).

Reference Material: For metals analysis, a standard reference material, oyster tissue (National Bureau of Standards, Standard Reference Material #1566a) was analyzed. This material is provided by the National Bureau of Standards and is exhaustively analyzed and its metals concentrations certified to be within a narrow range of values. Results showed high accuracy.

Method Blanks: Analysis of method blanks showed no laboratory contamination.

Table A-1 presents the schedule of analyses. Table A-2 presents the results of these different tests for metals. Recovery efficiency and precision measurements show control limit exceedence for several metals. The extracts were reanalyzed for arsenic, cadmium, and lead. The reanalysis also revealed some analytical problems. In the case of lead and cadmium, some of these problems may be related to the low concentrations of contaminants in relation to the detection limit. Though these quality control problems are not severe, the

APPENDIX (Continued)

arsenic, cadmium, and lead values are flagged with an E to denote estimated concentration. To better estimate the true concentrations of these metals, the two analyses were averaged to present one estimate of concentration.

Table A-3 shows results for pesticides. Table A-4 shows results for PAH and Table A-5 shows results for butyltins. Table A-6 reviews surrogate recovery data for all analyses. These analyses passed all quality assurance tests and can be used without further qualification.

Table A-1. Schedule of analyses.

Elapsed Days																
				Metals		Organics		Pesticides		Metals		Organics		Pesticides		
Lab	Site	Date	Collected	Date	Prepared	Date	Extracted	Analyzed	Date	Extracted	Analyzed	Date	Extracted	Analyzed	Date	
Number																
Fish																
438090	7	10/19/89		10/23/89		11/10-13/89		11/14-28/89		01/04/90		02/01/90		01/17/90		02/02/90
438091	8	10/19/89		10/23/89		11/10-13/89		11/14-28/89		01/04/90		01/18/90		01/17/90		02/02/90
438092	10	10/20/89		10/23/89		11/10-13/89		11/14-28/89		01/04/90		01/18/90		01/17/90		02/02/90
438093	11	10/20/89		10/23/89		11/10-13/89		11/14-28/89		01/04/90		01/18/90		01/17/90		02/02/90
408094	12	10/19/89		10/23/89		11/10-13/89		11/14-28/89		01/04/90		02/05/90		01/17/90		02/02/90
Clams																
438080	1	09/12/89		10/24/89		11/10-13/89		11/14-28/89		01/04/90		02/05/90		01/17/90		02/01/90
438081	2	09/12/89		10/24/89		11/10-13/89		11/14-28/89		01/04/90		01/18/90		01/17/90		02/01/90
438082	3	09/12/89		10/24/89		11/10-13/89		11/14-28/89		01/04/90		02/01/90		01/17/90		02/01/90
438083	4	09/12/89		10/24/89		11/10-13/89		11/14-28/89		01/04/90		01/17/90		01/17/90		02/02/90
438084	5	09/12/89		10/24/89		11/10-13/89		11/14-28/89		01/04/90		02/01/90		01/17/90		02/02/90
438085	6	09/12/89		10/24/89		11/10-13/89		11/14-28/89		01/04/90		01/17/90		01/17/90		02/02/90
438086	7	09/12/89		10/24/89		11/10-13/89		11/14-28/89		01/04/90		02/05/90		01/17/90		02/02/90
438087	8	09/12/89		10/24/89		11/10-13/89		11/14-28/89		01/04/90		02/05/90		01/17/90		02/02/90
Fish																
038205	7	09/21/90		1/16/91		--		--		02/04/91		02/27/91		02/04/91		03/06/91
038206	8	09/20/90		1/16/91		--		--		02/04/91		02/27/91		02/04/91		03/06/91
038207	12	09/20/90		1/16/91		--		--		02/04/91		02/28/91		02/04/91		03/06/91
038208	10	09/21/90		1/16/91		--		--		02/04/91		02/28/91		02/04/91		03/04/91
038209	11	09/21/90		1/16/91		--		--		02/04/91		02/28/91		02/04/91		03/04/91
Clams																
038210	3	01/15/91		1/16/91		--		--		02/04/91		02/28/91		02/04/91		03/05/91
038211	4	01/15/91		1/16/91		--		--		02/04/91		02/28/91		02/04/91		03/05/91
038212	6	01/15/91		1/16/91		--		--		02/04/91		02/28/91		02/04/91		03/04/91
038213	7	12/13/90		1/16/91		--		--		02/04/91		03/01/91		02/04/91		03/05/91
038214	8	12/13/90		1/16/91		--		--		02/04/91		03/01/91		02/04/91		03/05/91

Table A-3. Pesticide analysis quality control results.

	Percent spike recovery			
	Fish			Clams
	Site Num	11	11	3
	Lab Num	38208	38208	RPD
				38210
Aldrin		92	79	15
Chlordane		86	79	8
4,4'-DDT		95	76	22
Endosulfan I		89	75	17
Endrin		92	80	14
Heptachlor		92	79	15
gamma-BHC		92	77	18
Methoxychlor		89	75	17

RPD=Relative percent difference

Table A-4. PAH analysis quality control results.

	Matrix Spike - Percent Recovery						
	Site Num Lab Num	Fish			Clams		
		11 38208	11 38208	RPD	3 38210	3 38210	RPD
Napthalene		80	77	4	70	58	19
Acenaphthylene		91	90	1	86	87	1
Acenaphthene		88	87	1	82	75	9
Fluorene		88	87	1	80	80	0
Phenanthrene		92	87	6	85	81	5
Anthracene		89	84	6	75	73	3
Fluoranthene		95	89	7	68	75	10
Pyrene		90	85	6	93	84	10
Benzo(a)anthracene		85	83	2	85	85	0
Chrysene		85	83	2	80	84	5
Benzo(b)fluoranthene		92	90	2	82	82	0
Benzo(k)fluoranthene		84	86	2	79	82	4
Benzo(a)pyrene		87	84	4	77	75	3
Ideno(1,2,3-cd)pyrene		92	75	20	74	74	0
Dibenzo(a,h)anthracene		76	72	5	74	76	3
Benzo(ghi)perylene		61	53	14	61	49	22

RPD = Relative percent difference

Table A-5. Butyltins analysis quality results from Sinclair Inlet.

Site	% Spike recovery		RPD
	10	Duplicate	
Lab Number	438092	438092	
Tetrabutyltin	79.8	93.5	16%
Tributyltin	67.3	75.5	11%
Dibutyltin	70.5	65.8	7%
Monobutyltin	66.5	30.8	73%
Tripropyltin (surrogate)	82.4	82.4	0%

RPD = Relative Percent Difference

Table A-6. Recoveries of spiked surrogates for organics and organotins analysis.

Percent recovery of surrogate spike											
		Fish					Clams				
	Lab Number	8205	8206	8207	8208	8209	8210	8211	8212	8213	8214
	Site Number	7	8	10	11	12	3	4	6	7	8
<u>PAH Surrogates</u>											
2-Fluorobiphenyl		67	73	76	66	78	78	76	78	84	73
D14-Terphenyl		90	78	79	75	85	85	78	79	84	77
Pyrene-D10		91	76	74	69	80	78	72	73	81	73
<u>Pesticide Surrogates</u>											
4,4-Dibromooctafluorobiphenyl		86	84	92	96	67	94	83	75	88	108
Dibutylchlorendate		81	66	69	56	46	83	60	59	57	97
Octachloronaphthalene		37	35	33	39	17	36	42	33	22	54
	Lab Number	8090	8091	8092	8093		8082	8086	8087		
	Site Number	7	8	10	11		3	7	8		
<u>Butlytin Surrogate</u>											
Tripropyltin		74	64	86	76		75	90	14		

RPD = Relative Percent Difference

MANCHESTER ENVIRONMENTAL LABORATORY

7411 Beach Drive SE , Port Orchard Washington 98366

CASE NARRATIVE

March 12, 1990 ¹⁹⁹¹

Subject: Sinclair II and Bellingham Bay Bioaccumulation

Samples: 91 - 038205 to 91 - 038214 and 91 - 038215

Case No. DOE-902B
DOE-601C

Officer: James Cubbage

By: Dickey D. Huntamer *DDH*
Organic Analysis Unit

POLYNUCLEAR AROMATIC HYDROCARBONS

ANALYTICAL METHODS:

No official EPA method exists for semivolatile tissue analysis. The prepared tissue samples were extracted with a 50:50 mixture of methylene chloride and acetone using the Manchester modification of the EPA CLP and SW-846 Method 8270 procedure with capillary GC/MS analysis of the sample extracts. All CLP QA/QC procedures were performed on the samples. Since Polynuclear Aromatic Hydrocarbons (PAH) were the primary target analytes and low detection limits were desired sample cleanup using Gel Permeation Chromatography (GPC) at both 2000 Molecular Weight (MW) and 1000MW cutoff (SW-846 Method 3640) followed by Silica Gel cleanup Method 3630 was done on the samples. Lower Quantitation Limits were also realized by extracting approximately 50 grams of tissue and concentrating the final extract to 1.0 mL for analysis.

HOLDING TIMES:

Under Puget Sound Estuary Program (PSEP) Guidelines for organic compounds tissue samples can be stored frozen for up to one year before extraction. After collection samples were prepared for the laboratory by the field staff and stored frozen until extraction. Since the samples were stored frozen all sample extraction holding times were met. The reporting form for holding times indicates that the sample holding times were exceeded however this is not the case since it is measured from collection date and includes the time the samples were frozen. All analyses were performed within the specified 40 day holding time.

BLANKS:

No significant PAH blank contamination was detected.

SURROGATES:

The samples received all six surrogate compounds normally added to semivolatile analyses. Due to the silica gel cleanup only the non-polar surrogates Terphenyl-d14, Pyrene-d10 and 2-Fluorobiphenyl were recovered. Only one of these compounds, Pyrene-d10 is a true PAH compound and is representative of the PAH target analytes. Surrogate spike recoveries for all three compounds were within normal limits for CLP soil recovery limits. The CLP recovery limits are only advisory since no tissue surrogate spike recovery limits have been established.

MATRIX SPIKE AND MATRIX SPIKE DUPLICATE:

Matrix spikes compounds were added at 20 ug, rather than the normal spiking concentration of 50 ug, to approximate the low detection limits requested. No significant problems were encountered with recovering the matrix spike compounds at this level (400 ug/Kg wet weight). Although no matrix spike recovery limits have been established at this low level, spike recoveries were generally within the normal CLP recovery range found at higher matrix spike levels.

Two matrix spike and matrix spike duplicates (MS/MSD) were analyzed with the set. Samples 038208 and 038210 were used for the matrix spikes. Matrix spike recoveries ranged from 53 % to 95 % for 038208 and 49 % to 93 % for 038210. The Relative Percent Difference (RPD) ranged from 1 % to 14 % for 038208 and 0 % to 22 % for 038210.

SPECIAL ANALYTICAL PROBLEMS:

No analytical problems were encountered in the analysis. The low detection limits were achieved by extracting 50 grams of sample, cleaning up the extract using Gel Permeation Chromatography followed by Liquid Chromatography (silica gel) and concentrating the extract to 1.0 mL prior to analysis.

PESTICIDES / PCB

ANALYTICAL METHODS:

The tissue (clams and crabs) was extracted by the Manchester Laboratory using a Polytron tissue grinder and a 50:50 mixture of methylene chloride and acetone as the solvent. The analyses were done following EPA Method 8080 (chlorinated pesticides, PCB's using capillary Gas Chromatography/Electron Capture Detector (GC/ECD) analysis.

The percent lipid determination was performed in a similar fashion to the analytical extractions except petroleum ether was used as the solvent. The extract was evaporated and weighed to determine the extractable lipid. Percent solids were also determined on the samples. The results are given in the table below.

Lab Number	Percent Solids	Percent Lipids
038205	18.4	0.09
038206	16.7	0.10
038207	18.0	0.19
038208	19.3	0.0
038209	21.0	0.18
038210	12.1	0.19
038211	11.2	0.16
038212	11.8	0.44
038213	12.0	0.26
038214	11.8	0.18
038215	12.3	0.25

BLANKS:

No significant blank contamination was found.

HOLDING TIMES:

All samples were analyzed within the 40 day holding time.

SURROGATES:

Surrogate spike recoveries for the Pesticides/PCB's ranged from 17% to 108% for 4,4'-Dibromoocta-fluorobiphenyl (DBOB), Dibutylchlorendate (DBC) and Octachloronaphthalene (OCN). One surrogate, OCN is partially removed by the Florisil cleanup. No advisory surrogate recovery limits have been established for tissue samples. Consequently data qualifiers were not added to the data based on surrogate recoveries.

MATRIX SPIKE AND MATRIX SPIKE DUPLICATE:

Four matrix spikes were analyzed for pesticides to reflect the two different types of tissue (clam and fish) matrix effects. Recoveries of the pesticides ranged from 75% to 119%. The relative Percent Difference (RPD) ranged from 9% to 28%. No matrix spike recovery or RPD limits have been established for tissue samples.

SPECIAL ANALYTICAL PROBLEMS:

The pesticides were run on the tissue extracts first then the extract was cleaned up using sulfuric acid treatment. These acid treated extracts were then reanalyzed for PCB's thus allowing lower quantitation limits.

DATA QUALIFIER CODES:

- | | | |
|-----|---|---|
| U | - | The material was analyzed for, but was not detected. The associated numerical value is the sample quantitation limit. |
| J | - | The associated numerical value is an estimated quantity. |
| R | - | The data are unusable (compound may or may not be present). Resampling and reanalysis is necessary for verification. |
| NAR | - | No Analytical Result. |
| M | - | The compound was detected and confirmed but was not quantitated. |

WASHINGTON STATE DEPARTMENT OF ECOLOGY
MANCHESTER ENVIRONMENTAL LABORATORY
P.O. Box 307, Manchester, WA 98353

DATA REVIEW

April 3, 1990

PROJECT: Sinclair Bioaccum-reanalysis
SAMPLE NO: 438090 - 438094 Metals, tissue
438080 - 438088 Metals, tissue
LABORATORY: Analytical Resources, Inc.
333 Ninth Ave North
Seattle, WA 98109
By: Craig Smith, Chemist

Metals

Holding time: Analyses for all parameters were performed within the holding time limits.

Reagent Blank: No analytes were detected in the blank.

Matrix Spike: The targeted accuracy of matrix spikes is +/- 25% of the true value.
All parameters were within the targeted limits for both spikes, except for one of As(51%).

Laboratory Control Sample: All results were within the +/- 20% recovery control limits, except for As(76%), and Pb(50%).
In the case of Pb, after the sample was diluted to avoid the minimizing interferences, the amount of Pb in the diluted solution was about equal to the detection limit of the instrument. The same procedure for Cd gave a diluted concentration below the limit of detection.

Sample Duplicate: The target limits are +/- 20%, or +/- 1 detection limit for samples less than 5 times the detection limit.
All values were within the targeted limits.

Sample Data: The data is acceptable for use without qualification.

These tissue samples were originally prepared using a Nitric Acid/Perchloric Acid digestion. Interferences due to the presence of Perchloric Acid in the digested samples caused the results for As, Cd, and Pb to be questionable. Reanalysis was accomplished using Nitric Acid/Hydrogen Peroxide digestion.

WASHINGTON STATE DEPARTMENT OF ECOLOGY
MANCHESTER ENVIRONMENTAL LABORATORY
P.O. Box 307, Manchester, WA 98353

DATA REVIEW

January 9, 1990

PROJECT: Sinclair Bioaccumulation

SAMPLE NO: 438090 - 438094 Metals in fish tissue:
438080 - 438088 Metals in shellfish tissue:
Cu, Ag, As, Cd, Cr, Hg, Pb, Zn

LABORATORY: Analytical Resources, Inc.
333 Ninth Ave North
Seattle, WA 98109

By: Craig Smith, Chemist

The contract written for analysis required analysis be performed by Graphite Furnace. It was agreed that an ICP scan could be run on the samples to determine if any parameters were near the detection limits. Some results were reported using the ICP. These results are for specific parameters whose results do not lie near a detection limit.

The quality of results is O.K., but not as high as the laboratory would desire. The main problem is the use of the Nitric/Perchloric acid digestion, which is known to cause interferences in graphite furnace analysis. Better results for As, Pb, and Cd could be obtained if a Nitric acid/Hydrogen Peroxide digestion were used instead. Re-analysis of the samples for these three parameters is available at no extra cost.

Metals

Holding time: Analyses for all parameters were performed within the holding time limits.

Reagent Blank: The preparation blank showed no detectable analytes.

Matrix Spike: The targeted accuracy of matrix spikes is +/- 25% of the true value, for those samples whose concentrations are not greater than 4 times the amount of spike added. Two spikes were analyzed, one for the fish tissue and one for the shellfish tissue. In the case of the fish tissues, all recoveries were acceptable with the exception of Cadmium, at 128%. Arsenic and Lead spikes were not valid because the background concentrations were greater than 4 times the added amount of matrix spike. For the shellfish, only Cadmium at 128%, and Lead at 52%, were not acceptable. (see note above)

Laboratory Control Sample: All results of DORM-1 were within the +/- 20% recovery control limits with the exception of Lead at 150%. The level of Lead is about 2 times the IDL (instrument detection limit). It would not be reasonable to expect quantitation of the sample within +/- 20% at that low a concentration (used GFAA).

Sample Duplicate: The target limits are +/- 20% relative percent difference (RPD) for those samples whose concentrations exceed a level of 5 times the IDL, otherwise the control limit is +/- 1 detection limit. Two separate duplicates were analyzed. In the case of the fish tissue, limits were met with the exception of Chromium, Lead, and Silver (see results enclosed). In the case of shellfish tissue, limits were met with the exception of Arsenic, Chromium, and Lead (see results enclosed).

Sample Data: The data is acceptable, with a "J" value attached to Lead and Chromium.

I have requested the re-analysis for Arsenic, Lead, and Cadmium.